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REACTION AND PROTECTION OF ELECTRICAL WIRE INSULATORS IN ATOMIC-OXYGEN ENVIRONMENTS

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SUMMARY

Atomic-oxygen erosion on spacecraft in low Earth orbit is an issue which is becoming increasingly important because of the growing number of spacecraft that will fly in the orbits which have high concentrations of atomic oxygen. In this investigation, the atomic-oxygen durability of three types of electrical wire insulation (carbon-based, fluoropolymer, and polysiloxane elastomer) were evaluated. These insulation materials were exposed to thermal-energy atomic oxygen, which was obtained by RF excitation of air at a pressure of 11-20 Pa. The effects of atomic-oxygen exposure on insulation materials indicate that all carbon-based materials erode at about the same rate as polyamide Kapton and, therefore, are not atomic-oxygen durable. However, the durability of fluoropolymers needs to be evaluated on a case-by-case basis because the erosion rates of fluoropolymers vary widely. For example, experimental data suggest the formation of atomic fluorine during atomic-oxygen amorphous-fluorocarbon reactions. Dimethyl polysiloxanes (silicone) do not lose mass during atomic-oxygen exposure, but develop silica surfaces which are under tension and frequently crack as a result of loss of methyl groups. However, if the silicone sample surfaces were properly pre-treated to provide a certain roughness, atomic oxygen exposure resulted in a sturdy, non-cracked atomic-oxygen durable SiO_2 layer. Since the surface does not crack during such silicone-atomic oxygen reaction, the crack-induced contamination by silicone can be reduced or completely stopped. Therefore, with proper pre-treatment, silicone can be either a wire insulation material or a coating on wire insulation materials to provide atomic-oxygen durability.

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INTRODUCTION

Spacecraft in low Earth orbit (180 to 650 km) are subject to attack by atomic oxygen (Ref. 1 and 2). Electrical insulation of wires for spacecraft occupying this altitude must be resistant to or protected from atomic oxygen. Most, if not all, organic insulative coatings are not resistant to atomic oxygen and must be externally protected from the low Earth orbit environment. Currently, this is done either by isolating wires in aluminum tray or conduit or by routing wires to other areas that are protected from atomic oxygen. This approach not only adds excess weight to the orbiting system, but also decreases design flexibility.

This problem becomes most critical at the low altitudes occupied by some Earth-observing systems (used for remote imaging and gathering data about earth from space) because the atomic-oxygen density increases with decreasing altitude (Ref. 3). For example, the spacecraft recently designed for the TRMM (Tropical Rainfall Measurement Mission) spacecraft will be at an altitude of 350 km. According to the gas concentration-altitude relation shown in Figure 1, the atomic-oxygen density and, therefore, the flux on this spacecraft, will be about twice the values to be encountered by International Space Station Alpha (410-450 km altitude).

The ideal material to be used as an electrical wire insulator for space applications should be able to overcome the problem described above. That is, in addition to the qualifications that must be met for all electrical-wire insulating materials on Earth (low flammability, low arc tracking probability, high electrical resistivity, high dielectric strength, and light weight), it should also meet the qualifications for flexibility, outgassing in vacuum, and atomic-oxygen durability.

The objective of this investigation was to determine if commercially available electrical wire insulating materials meet or can be modified to meet the qualifications listed above. The approach has been to first, examine the reaction between atomic oxygen and currently available wire insulating materials and second, to explore the possibility of modifying these materials to meet the necessary qualifications.

LITERATURE REVIEW ON EROSION OF WIRE INSULATING MATERIAL

One of the polymers most frequently used as an electrical-wire insulator for space application, polyamide Kapton, is oxidized and thus eroded by atomic oxygen. All other carbon-based insulating materials react with atomic oxygen in the same manner. The erosion yield of Kapton, or its volume loss per atom caused by atomic oxygen at 4.5 eV kinetic energy, is 3×10^{-24} cm^3/atom (Ref. 2). Based on this value, one can predict that a Kapton thickness of 0.1mm will vanish in about 400 days if it is exposed to the average flux expected to be encountered by the Space Station, and a thickness of 1mm will vanish in about 3 years if the maximum expected flux is used for the calculation. It is, therefore, necessary that Kapton

be externally protected from atomic oxygen if it is to be used in low Earth orbit.

Fluoropolymer electrical-wire insulators, frequently used for space applications, have a wide reported range of erosion-yield values, 0.03 to 0.5×10^{-24} cm^3/atom (Ref. 2).

Polysiloxane elastomers (silicone rubbers), are commonly used for electrical-wire insulation on Earth and have been proposed as potential insulative wire-coating materials for space applications. Some of the desirable properties of these materials include flexibility over a wide temperature range, light weight, oxidative stability (not readily oxidized in water or air), and satisfactory dielectric properties. Also, it was previously determined that exposing silicone rubber to atomic oxygen converts the exposed silicone surface into an atomic-oxygen-resistant silica surface layer, and the surface layer thus formed protects the underlying materials from further atomic oxygen attack. However, questions about the effectiveness of this surface layer as an atomic oxygen barrier arose when some surface phenomena were observed. The observations included surface-layer cracks, a result of surface shrinkage from silicone oxidation, and potential oxygen diffusion from the surface to the silicone interior (Ref. 4 and 5). In addition, observed contamination from the silicone atomic-oxygen reactions can give rise to further problems concerning using silicone in low Earth orbit (Ref. 4). To address these issues and further explore the possibility of using silicone rubber to protect electrical wires against atomic oxygen, ground-laboratory experiments were conducted and are described in this report.

EXPERIMENTAL METHOD
Carbon-based wire-insulating materials, fluoropolymers and silicone samples were exposed to an atomic-oxygen rich environment generated by an SPI Plasma-Prep II, Model 11005, RF plasma asher to assess their atomic-oxygen durability. All materials tested were subjected to an air plasma at a pressure of 11-20 Pa (80 to 140 millitorr). The reaction-chamber volume was 1300 cm^3 (1.3 liters).

The atomic oxygen to be encountered by Space Station has an impact energy of 4.5 eV and a flux of 1.0×10^{14} atoms/[(cm^2)(sec)]. This compares to the values of 0.04 eV for thermal energy and much higher but unknown actual flux, respectively, for the atomic oxygen generated in the RF plasma asher.

In order to correlate the effects of erosion of the above two different energy levels of atomic oxygen, polyamide Kapton H witness coupons were simultaneously ashed with every sample tested in the asher. The mass loss of the Kapton witness coupon during ashing, together with its surface area, its density of 1.42 g/cm^3, and its erosion yield value of 3.0×10^{24} cm^3/atom for 4.5 eV atomic oxygen, were used to calculate the "Kapton effective fluence", or

the number of collisions (between 4.5 eV atomic oxygen in space and unit surface area of Kapton) needed to produce the observed Kapton mass loss observed in the RF plasma asher.

The term "Kapton effective fluence" will be used throughout the remainder of this report. Also, for the asher used in this research, the "Kapton effective flux", or rate of the collision described above, was calculated to be in the $3.5-5.3 \times 10^{15}$ atoms/[$(cm^2)(sec)$] range.

Previous results have shown that data collected from atomic-oxygen durability testing in RF plasma ashers agree qualitatively with data obtained from space experiments. However, space atomic oxygen was found to be less erosive to PTFE and FEP than polyamide Kapton, but the atomic oxygen generated by RF plasma asher was found to be about equally erosive to PTFE, FEP, and polyamide Kapton. The reason for such exception is not known at this time.

The carbon-based wire-insulating materials evaluated include Apical (Allied-Apical Co.,polyamide), Upilex R and Upilex S (ICI Americas,Inc., polyamide), PEEK (ICI Americas, Inc., polyetherether ketone), Nomex 410 and Nomex 418 (Du Pont, aramid papers made from synthetic aromatic polyamide polymers), and Voltex 450 (Lydall, Inc., composed of aramid fiber and neoprene binder) (Ref. 6 and 7). The fluoropolymers evaluated include FEP, PTFE, and Teflon AF [Du Pont, amorphous copolymers of perfluoro(2,2-dimethyl-1,3-dioxole) and tetrafluoroethylene]. Silicones evaluated include Dow Corning DC93-500, NuSil Technology CV2942, and NuSil Technology CV2942 containing alumina. These silicones are all classified as dimethyl polysiloxane elastomers. The DC93-500 samples were prepared, according to instructions issued by Dow Corning, in the laboratory at National Aeronautics and Space Administration Lewis Research Center. The CV2942 samples were prepared by NuSil Technology.

Three Kapton witness coupons were used in the process of evaluating each insulating material. The coupons were ashed, before, after, and along with each sample. The mass loss and appearance of the witness coupons were used to calculate the change in flux and to detect possible contamination resulting from the insulating materials presence in the atomic-oxygen environment. The erosion yield of each material relative to Kapton was also calculated.

Since the mass loss of silicone rubber that resulted from ashing was small, additional experiments were conducted to assess their atomic oxygen durability and suitability as a wire-insulating material. These are described in the following two paragraphs.

The experimental design is shown in Figure 2. For each experimental run, a silicone layer with a smooth surface (thickness between 12.7um and 1.1mm) was used to "protect" a piece of polyamide Kapton (approximate mass 25mg) from direct atomic oxygen contact in the

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plasma asher. Excellent protection resulted if the silicone surface not directly exposed to the plasma did not change, and if the underlying Kapton sample was found to have negligible mass loss after the exposure period. Each silicone sample was characterized by optical microscopy, surface profilometry (to detect changes in surface morphology), and ESCA analysis (to detect and quantify changes in chemical composition of the exposed and non-exposed surfaces) before and after exposure.

The possibility of enhancing the ability of silicone to resist atomic oxygen was also explored. This work was prompted by observations of surface roughness effects during preliminary ashing experiments of NuSil Technology's CV2187 silicone. To explore this phenomenon, silicone samples of identical chemical composition but different surface roughness were prepared, ashed and analyzed. At NuSil Technology, different surface morphologies were obtained by curing at high pressure on release papers that varied in surface roughness (Ref. 8). At National Aeronautics and Space Administration Lewis Research Center, Dow Corning DC93-500 samples with rough surfaces were prepared by curing at 1 atm pressure on surfaces that were prepared by ashing or ion beam texturing of Kapton, PTFE, or FEP. Samples having smooth surfaces, on the other hand, were obtained by curing on smooth silicon wafers. Using optical microscope, profilometer, and ESCA analysis, both pristine and ashed samples with different surface morphologies were characterized and compared before and after atomic-oxygen exposure.

RESULTS AND DISCUSSION

Carbon-based insulators

The carbon-based polymers to polyamide Kapton erosion yield ratios were calculated by comparing the mass loss of the carbon-based polymer to the mass loss of the Kapton witness coupons ashed simultaneously. The calculated relative erosion-yield values of the carbon-based insulating materials are summarized in Table 1 and show that the erosion yield of carbon-based electrical-insulating materials range from 21% to 141% of the Kapton value. Knowing the results obtained from this ground test facility agrees qualitatively with the results obtained from space experiments, and knowing Kapton is not durable in low-Earth orbit, the data described above indicate that carbon-based materials are susceptible to degradation and, therefore, must be externally protected if they are to be used in the low-earth-orbit atomic-oxygen environment.

Fluoropolymers

The fluoropolymers were also found to be susceptible to degradation in an atomic-oxygen environment. Table 2 shows the mass-loss rates and the relative erosion yields of the PTFE, FEP, and Teflon AF2400 (an amorphous fluoropolymer) samples ashed at about 12 Pa (0.08-0.09 Torr). The mass loss rates of all Kapton samples ashed

immediately before and simultaneously with the fluoropolymer are also included in this table.

It was observed that when Teflon AF2400 was exposed to the plasma, the pressure in the asher was higher than normal, and the plasma became brighter and much more reactive. In particular, it was observed that the mass-loss rate of Kapton increased approximately 800% if a 2.54 cm diameter, 0.1 mm thick Teflon AF2400 sample was also present in the reaction chamber (volume $1300cm^3$ or 1.3 liters). In addition, it was observed that the mass-loss rate for Teflon AF2400 was much higher than the mass-loss rate of all other materials evaluated, including the Kapton ashed simultaneously with Teflon AF2400.

Based on the pressure gauge reading, it was concluded that the presence of Teflon AF2400 in the reaction chamber caused the pressure contribution of the plasma and, therefore, the plasma flux to increase significantly. However, the increase in plasma flux is estimated to be much less than the 800% increase in Kapton mass-loss rate. It is believed that other factors, such as the presence of the much more corrosive atomic fluorine in the plasma, also contributed to the large increase of mass-loss rate.

Such a large enhancement of erosion by a material on nearby samples has never been observed before. Specifically, it was not observed for the other two fluoropolymers (PTFE or FEP) examined in this research. However, a 2.54 cm diameter Kapton sample was found to be ashed 145-180% faster if it was surrounded by a large quantity of FEP. In addition, after ashing, contamination of Kapton was observed (i.e., sample surfaces became gray).

The high mass-loss rate for Kapton during Kapton-Teflon AF2400 simultaneous ashing suggests the possibility that this fluoropolymer causes the production of atomic fluorine to be present along with high flux of atomic oxygen. This indicates that the presence of some fluoropolymers will cause enhanced degradation of neighboring hydrocarbon polymers in an atomic oxygen environment, especially if they are in the close proximity of each other. For example, consider a material consisting of Teflon AF2400 protected by an oxide coating having a pinhole. When exposed to atomic oxygen, Teflon AF2400 would be eroded at the pinhole point, producing high flux and atomic fluorine. Consequently, the protective coating could also be eroded if it reacts with fluorine, causing undesirable results.

The high erosion rate and the enhanced degradation of the neighboring materials described above were not obvious when the other two fluoropolymer samples (PTFE and FEP) were exposed to atomic oxygen. This, and the previously reported fact that space atomic oxygen is less erosive to fluoropolymer than the asher atomic oxygen, suggests that fluoropolymer atomic-oxygen reactions

are complicated and not well understood. Therefore, every individual fluoropolymer needs to be closely examined before it can be used as an electrical-wire insulating material in low earth orbit.

Silicones

Kapton mass-loss data from experiments (Figure 2) conducted to determine the ability of silicone to protect Kapton in an atomic-oxygen environment are summarized in Table 3. Based on mass-loss measurements of protected Kapton during control runs (10 to 30 ug), where conditions were identical except that the atomic-oxygen fluence was zero, we believe that the mass loss of protected Kapton samples included in this table are within experimental error. Optical micrographs show that only the silicone surfaces directly exposed to the plasma form cracks (Figure 3). The chemical composition of both surfaces of the silicone samples exposed to higher fluences were measured by ESCA analysis (Table 4). This data shows that the chemical composition of the surface not directly exposed to atomic oxygen does not change.

Based on this data, we conclude that the 0.0127mm thick layers of silicone tested are adequate to protect polymers against atomic oxygen up to a Kapton effective fluence of $1.2x10^{21}$ atoms/cm^2. Also, the 0.5mm thick silicone samples tested are adequate to protect polymers against a thermal-energy atomic-oxygen Kapton effective fluence of up to $1.0x10^{22}$ atoms/cm^2. For reference, $1.2x10^{21}$ atoms/cm^2 is the average fluence expected to be encountered by the Space Station during a 3-month period, and $1.0x10^{22}$ atoms/cm^2 is the average fluence expected to be encountered by the Space Station during a 3-year period.

Though the above results show that a thickness of 0.0127mm is adequate for atomic-oxygen protection, it may be possible to use thinner coatings. However, it needs to be much thicker than 2000Å, since previous results have shown the oxygen diffusion depth to be 1000Å, 2000Å, and >>2000Å for Kapton effective atomic-oxygen fluences on the order of $5x10^{19}$, $5x10^{20}$, and $5x10^{21}$ atoms/cm^2, respectively (Ref.5).

In addition to data in Tables 3 and 4, the following observations for the experimental runs are noted. First, the Kapton sample protected by a 0.5mm thick DC93-500 silicone layer and exposed to an atomic-oxygen fluence of $1.0x10^{22}$ discolored and increased in mass (63ug, 0.3% of original mass of 21mg). This is believed to be contamination and even though the mass data suggests that amount is small, its source is unknown. Second, it is noted that all samples except the 12.7um thick NuSil Technology sample developed cracks (Figure 3) on the exposed surfaces, which were smooth prior to exposure. It is further noted that, all NuSil Technology samples developed waves (Figure 4), not cracks, when exposed to atomic oxygen.

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The wavy morphology (Figure 4) described above may be the result of a compressive stress on the surface of all samples made by NuSil Technology. Such surface compression on these samples was likely because they were cured at high pressure. More studies are needed to test and confirm this hypothesis.

The surface crack (Figure 3), on the other hand, is known to be the result of surface shrinkage during atomic oxygen exposure. However, the effect of surface morphology on the surface crack has not been studied previously. It was observed in this research that the extent of surface cracking resulting from atomic-oxygen exposure was reduced or completely avoided when the surface was rough. This phenomena and its implications are discussed later in this report.

The silicone mass loss, resulting from atomic-oxygen exposure, was found to be less than the experimental error of the measuring instruments. Therefore, the erosion yields calculated from mass loss data are close to zero. Based on this data, silicone appears more durable than polyamides or fluoropolymers in an atomic-oxygen environment, and that the ability of silicone to protect polymers against atomic oxygen depends entirely on the depth of surface cracks and depth of oxygen diffusion from the surface into the silicone interior. Any method that would reduce or stop surface cracking and/or oxygen diffusion would enhance the ability of silicone to protect polymers from atomic oxygen.

Ideally, if the mechanisms of both surface layer cracking and oxygen diffusion into the silicone interior were known, the methods to prevent these from happening could be developed, and the ability of silicone to protect polymers from atomic oxygen could be enhanced. At this time, however, there is not a clear mechanism to explain all observed phenomena. Specifically, the wavy morphology of the NuSil Technology silicone samples (Figure 4) can only be hypothesized as above, but can not be satisfactorily explained by any suggested mechanism.

A mechanism, however, is suggested to explain surface cracking and the above-described phenomenon that rougher surfaces crack less when exposed to atomic oxygen. Surface cracking is believed to be due to tensile stress at the surface caused by the surface shrinkage during atomic oxygen exposure. Just below the cracked surface is a "transition region" that, through its depth, the shrinkage caused by atomic oxygen changes from that of the surface to that of pristine silicone (i.e., zero). A result of such gradual decrease of shrinkage magnitude through the thickness of the transition region is that the stress caused by surface shrinkage can at least partly be absorbed by the transition region, especially if the silicone is soft (i.e., low in durometer hardness). Therefore, the surface stress increase can be a result of a shrinkage magnitude increase, a transition region thickness decrease, and/or a durometer hardness decrease.

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When silicone with a smooth surface is exposed to atomic oxygen, the surface is quickly converted to a thin flat silicate layer before a notable amount of oxygen can diffuse into the interior. This conversion is accompanied by a significant surface shrinkage and a very thin "transition region". Consequently, stress caused by surface shrinkage exceeds the combined limit of what can be absorbed by the transition region and what can be withstood by the surface. The surface and part of the transition region is therefore pulled apart, causing cracking of the surface. The shockwave produced at the instant of cracking could result in further cracking if the crack formation is abrupt. However, as the atomic oxygen exposure continues after such cracking, the surface stress is reduced due to the morphology changes and the increasing thickness of the transition region with further atomic oxygen exposure. Therefore, further cracking at the original silicone surface slows down. However, at the position where cracks are formed, pristine silicone is exposed to atomic oxygen and leads to further cracking at this location.

If the silicone sample is very small, the total shrinkage of the small and smooth surface may be too small to generate a surface stress enough to cause surface cracks. In this case, at least theoretically, no crack of the sample could happen. This "threshold area" of the sample has not been studied experimentally, but is believed to be about the same as the smallest area surrounded by the cracked line on a smooth silicone surface which had been exposed to a high fluence of atomic oxygen.

The concept of "threshold area" described above will be used greatly later in this report. This term, together with the term "threshold length", which is defined as the diameter of a circle whose area is the same as that of the "threshold area", will be used in a semi-quantitative analysis.

When a rough silicone surface is exposed to atomic oxygen it also forms a shrunk surface and a partly shrunk transition region. However, unlike the flat, one dimensional surface described above, the rough surface has a three-dimensional wavy shape (Figure 5(a)). For this case, the stress resulting from shrinkage does not always pull surface apart, but rather is partly released by flattening of the surface. Therefore, the chemical composition of the surface has a chance to approach its final configuration without cracking. Once this configuration is obtained without cracking, further silicone-atomic oxygen reaction is not expected to continue since the final composition is comparable to silica, which is an ideal atomic oxygen barrier.

Quantitative analysis to study the relation and magnitudes of surface stress, surface deformation, or the possibility of crack on a rough silicone surface is complicated. Major efforts are apparently needed to accomplish this. For practical purposes, in order to have a quantitative guideline on how rough the surface has

to be to avoid cracking, a semi-quantitative analysis on this subject is inferred and described in the following paragraph.

The rough surface of a silicone sample to be exposed to atomic oxygen can be considered as an assembly of a number of near-flat surfaces. For example, the rough surface described in the left half of Figure 5(a) is the same as the assembly of 9 near-flat surfaces (AB, BC, CD, to IJ). If the assembly of near-flat surfaces representing a "rough" surface can include at least one near-flat surface larger than the "threshold area" described 3 paragraphs before, then the rough surface is considered not rough enough because the large near-flat area will experience a stress which is big enough to cause cracks.

Another obvious parameter that characterizes the surface roughness is that the oxygen penetration depth (i.e., the thickness of the surface and transition region combined) needs to be smaller than the height of the surface roughness. Otherwise, the shrinkage and the stress thus resulted would go to the region under the rough part of the surface, and the role of the rough surface would disappear.

In summary, for a rough silicone surface to be an effective atomic oxygen barrier, the roughness needs to be: (1) curved enough so that it does not contain any near-flat surface that is as big as or bigger than the "threshold area" which is defined earlier in this report, and (2) tall enough so that the oxygen cannot diffuse to the region under the rough part of the surface.

If the term "peaks" is used to describe surface roughness, then, according to the above-described criteria, the silicone surface needs to meet the following conditions in order to be a good atomic oxygen barrier:

(1) The entire surface has to be covered by "peaks,"

(2) The peak width has an upper limit so that no peak may contain a near-flat surface area which may be larger than the "threshold area" of the sample (e.g.,AB, DE, and GH described in Figure 5(a)).

(3) There is no apparent lower limit for peak width.

(4) All peaks on the surface need to be taller than the transition region thickness, otherwise oxygen can diffuse through all of the peaks on the surface, and the surface is considered flat.

(5) In the scenario where the peaks become taller than the "threshold length", then the shrinkage may cause the peak itself to crack. This is not desirable. However, this scenario is unlikely to happen, at least for the types of process and product described in this report.

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A convenient guideline which includes all the conditions described above is: To avoid cracks during atomic oxygen exposure, the rough surface can be designed so that it is completely covered by peaks which are taller than the depth of the oxygen penetration, but narrower and shorter than the "threshold length" below which a smooth sample would not crack.

The above criteria suggest peak height and width ranges within which the rough surface of the silicone samples would not crack upon atomic oxygen exposure. However, what numbers in those ranges will result in the strongest surface under the least stress cannot be obtained from the analysis described above. Extensive theoretical and experimental study is needed if such an "optimum condition" is desirable.

Data illustrating effects of surface morphology on the silicone atomic-oxygen reaction are summarized in Table 5 and Figure 6. The following observations for DC93-500 silicone samples are noted.

- Atomic-oxygen exposure did not cause the rough silicone surfaces (obtained by curing on ion-beam textured PTFE and ion-beam textured Kapton) to crack, but did result in extensive cracking of the smooth silicone surface, obtained by curing on a silicon wafer.

- ESCA data shows that after atomic-oxygen exposure, the chemical composition of rough surfaces is much closer to SiO_2 than smooth surfaces.

- The sample cured on a textured Si wafer illustrates the importance of narrow peaks on the surface. This sample cracked during atomic-oxygen exposure even though the peaks on the surface were high. We believe that because the wide peaks (20-$70\mu m$, see Figure 5(b)) contain large near-flat areas, the shrink-induced stress on these areas behaved as if the surface was flat. It therefore caused surface cracks.

- The sample cured on ion beam textured Kapton had very high peaks which were much narrower than those described above. This sample did not crack. In fact, extensive mechanical abuses (i.e., quickly twisted by hands and tapping with hammer) caused only small cracks observable on its optical micrographs (Figure 7). Also, the oxygen to silicon ratio of this sample was 2.0, the same as SiO_2.

Because surface cracks render the silicone interior susceptible to additional atomic-oxygen attack and SiO_2 is an ideal atomic-oxygen barrier, the ability of silicone to protect polymers against atomic oxygen could be enhanced by controlling the morphology of the silicone surface. Based on observations for the DC93-500 samples,

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a surface which has peaks between 1 to 10μm wide and 50 to 3000Å high is ideal. For comparison, a typical small area surrounded by crack lines on the surface of a silicone sample (which had a smooth surface when pristine and had been exposed to 1.0×10^{22} atom/cm^2 of atomic oxygen) had a diameter of about 25 microns. In other words, DC93-500 has 25 microns as its threshold length below which a smooth sample does not crack.

Further work is needed to fully accomplish the objectives of this research. The process to mass-produce insulated wires protected by silicone with appropriate surface morphologies needs to be explored and developed. Most importantly, those silicones which are found to adequately protect polymers in the RF asher environment need to be tested in space to validate durability.

CONCLUSIONS

Atomic-oxygen durability of three types of wire insulating materials, i.e., carbon-based material, fluoropolymer, and silicones, were evaluated.

Among the carbon-based materials tested in the simulated atomic-oxygen environment, the rates of erosion caused by atomic oxygen were estimated to be 21% to 141% of the Kapton erosion rates, which has an average value of 0.1mm in about 400 days at the Space Station altitude (450Km), and much more at lower altitude. This result agrees with previous reports that carbon-based materials are susceptible to degradation and, therefore, must be externally protected if they are to be used in the low-Earth orbit atomic-oxygen environment.

The reactions of fluoropolymers to atomic oxygen vary widely from case to case and are sometimes unpredictable. For example, an amorphous fluoropolymer was observed to not only erode much faster than Kapton in an RF plasma asher, but to also greatly enhance the erosion of the neighboring materials. PTFE and FEP, on the other hand, were found to erode at about the same rates as Kapton in ground laboratory tests, but to erode much slower than Kapton in previous space-exposure tests. The fluoropolymer atomic-oxygen reactions are complicated. Therefore, fluoropolymers need to be evaluated on an individual case-to-case basis to determine the effects of atomic-oxygen exposure.

The "space-qualified" silicones (dimethyl polysiloxane elastomers) were the only samples in this study that did not have mass loss upon atomic-oxygen exposure. However, such exposure caused the surface composition to approach that of SiO_2. It also caused smooth surfaces to shrink and crack, which is considered to be the major contributor of contamination of the neighboring materials. Cracks and the chemical-composition changes were found to be limited to a layer of less than $12.7\mu m$ thick after 1.2×10^{21} atom/cm^2 atomic oxygen exposure. Surface cracks were found to be reduced or completely eliminated, and surface composition approached that of SiO_2 if the silicone surfaces were initially rough. A proposed mechanism of surface reactions suggests that shrinkage causes smooth surfaces to pull apart and rough surfaces to flatten. To avoid cracks during atomic oxygen exposure, the rough surface can be designed so that it is completely covered by peaks which are taller than the depth of the oxygen penetration, but more densely spaced and shorter than the "threshold length" below which a smooth sample would not crack. The proposed mechanism and the data obtained in this research suggest that silicones with properly controlled surface morphology may potentially be useful as wire insulators or coatings of wire insulators that will be subjected to atomic oxygen.

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TABLE 1.—THE EROSION YIELD VALUES FOR THE
CARBON-BASED INSULATING MATERIALS IN THERMAL
ENERGY ATOMIC OXYGEN ENVIRONMENT

	Density, g/cm^3	Weight loss/area relative to Kapton	Erosion yield relative to Kapton[a]
Apical polyimide	1.42	0.86	0.86
Upilex R polyimide	1.47	0.72	0.70
Upilex S polyimide	1.47	0.74	0.71
PEEK polyetherether ketone	1.26	1.25	1.41
Nomex 410 aramid papers (0.05 mm thick)	1.38	(b)	(b)
Nomex 418 aramid papers (0.075 mm thick)	1.38	0.20	0.21
Voltex 450 aramid fiber and neoprene binder	1.6	0.24	0.21

[a]Erosion yield of Kapton is 3.0×10^{-24} atom/cm^3 in 4.5 eV atomic oxygen environment.

[b]The 4.5 cm × 3.2 cm, 0.05 mm thick Nomex sample was ashed to small pieces of fragile and black materials by a Kapton effective fluence of 5.0×10^{20} atom/cm^2.

TABLE 2.—EFFECT OF FLUOROPOLYMERS ON KAPTON EROSION
YIELD[a]

	FEP Teflon	PTFE	Teflon AF2400
Kapton Mass Loss Rate[b] ashed without Fluoropolymer Present (μg/min)	5.275	4.985	1.017
Kapton Mass Loss Rate ashed with Fluoropolymer Present (μg/min)	5.958	6.267	8.975
Fluoropolymer Mass Loss Rate (μg/min)	6.908	5.917	33.293
Relative Mass Loss Rate (Kapton with Fluoropolymer)/(Kapton without Fluoropolymer)	1.129	1.264	8.825
Relative Mass Loss Rate (Fluoropolymer/ Kapton) during Kapton and Fluoropolymer Simultaneous Ashing	1.159	0.994	3.709
Erosion Yield Fluoropolymer Relative to Kapton	0.789	0.662	3.251

[a]All samples used in these experiments were disks having 2.5 cm diameter.
[b]In these experiments the atomic oxygen flux was kept at minimum levels by properly adjusting the asher settings. The three samples described here were ashed at different atomic oxygen fluxes. However, for every sample, the simultaneous fluoropolymer/Kapton ashing was conducted immediately after the Kapton (alone) ashing without changing any flux-associated settings.

TABLE 3.—WEIGHT LOSS OF THE 0.13 MM THICK,
0.025 G KAPTON SAMPLES PROTECTED BY
SILICONE IN THERMAL ENERGY ATOMIC
OXYGEN ENVIRONMENT

Sample type[a]	Sample thickness, mm	Kapton effective fluence, atoms/cm^2	Kapton sample mass loss, μG
DC93-500	0.5	2.8×10^{20}	8
DC93-500	0.5	1.1×10^{21}	38
DC93-500	1.0	1.1×10^{21}	17
DC93-500	0.5	1.0×10^{22}	-63[b] (weight gain)
CV2187 10% Al$_2$O$_3$	0.0127	1.2×10^{21}	25[b]

[a]The DC93-500 samples were Dow Corning product
cured at NASA Lewis Research Center. The CV2187
sample with 10% Al$_2$O$_3$ was prepared and cured by
McGhan NuSil Company.

[b]Some discoloration of these "protected" Kapton samples
are observed. The reason for the decoloration is not
known.

TABLE 4.—CHEMICAL COMPOSITION FOR PRISTINE AND ATOMIC OXYGEN
EXPOSED SILICONE SURFACES

Sample type	Sample thickness, mm	Kapton effective fluence, atoms/cm^2	Atomic oxygen exposure[a]	Surface composition						
				Si	C	O	P	B	N	F
Smooth DC93-500	0.5	1.1×10^{21}	Zero	25	45	30	0	0	0	0
			Indirect	24	46	30	0	0	0.1	0
			Direct	27	27	44	0	0.8	0.1	0
Smooth DC93-500	0.5	1.0×10^{22}	Zero	24	46	29	0	0	0	0
			Indirect	25	46	30	0	0	0	0
			Direct	26	27	47	0.2	0	0	0
Rough[b] DC93-500	0.75	1.5×10^{21}	Zero	22	52	26	0	0	0	0
			Direct	28	13	57	0	0	1	0.7
Smooth CV2187	0.0127	1.2×10^{21}	Zero	24	47	29	0	0	0	0
			Indirect	24	47	29	0	0	0	0
			Direct	25	41	33	1.1	0	0	0

[a]The atomic oxygen exposure is zero if the pristine surface is examined, indirect if the
samples are ashed but the surfaces are not directly exposed to atomic oxygen, and direct
if the samples are ashed and the surfaces are directly exposed to atomic oxygen (Fig. 2).
[b]The rough surface silicone was made by curing on an ion beam textured Kapton substrate.

TABLE 5.—EFFECT OF SILICONE SURFACE ROUGHNESS ON THE SILICONE-ATOMIC OXYGEN REACTION

Silicone type	Curing substrate	Surface before ashing		Kapton effective fluence, 10^{21} atom/cm^2	Ashed surface	
		Peak width, μm	Peak height, Å		Cracks	O/Si ratio
DC93-500	Smooth Si wafer	-----	-------	1.1	yes	1.6
DC93-500	Smooth Si wafer	-----	-------	10	yes	1.8
DC93-500	Textured Si wafer	20-70	2000-6000	0.48	yes	---
DC93-500	Ashed Kapton	0.1-2	5-100	0.41	yes	---
DC93-500	Ion beam textured FEP	0.2-2	10-200	0.48	yes	---
DC93-500	Ion beam textured PTFE	0.8-3	50-800	0.48	no	1.9
DC93-500	Ion beam textured Kapton	2-3	1500-3000	1.5	no	2.0
DC2942	Release paper	2-7	50-1000	2.1	no	1.5
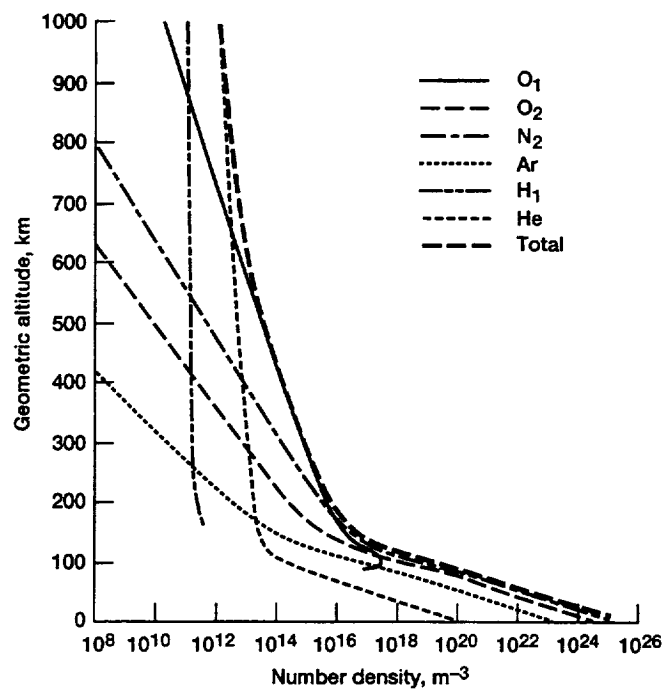
Figure 1.—Number density of individual species and total number density as a function of geometric altitude (from Ref. 3).

(Top view)

(Side view)
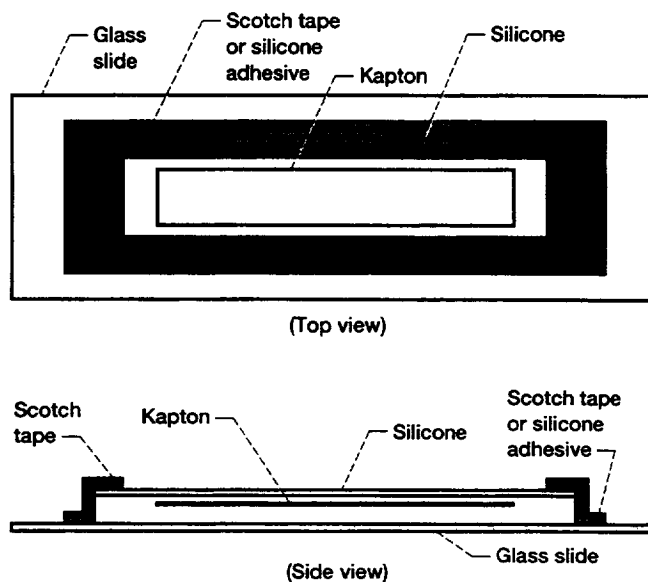
Figure 2.—Experimental design to determine the ability of silicone to protect Kapton against atomic oxygen.
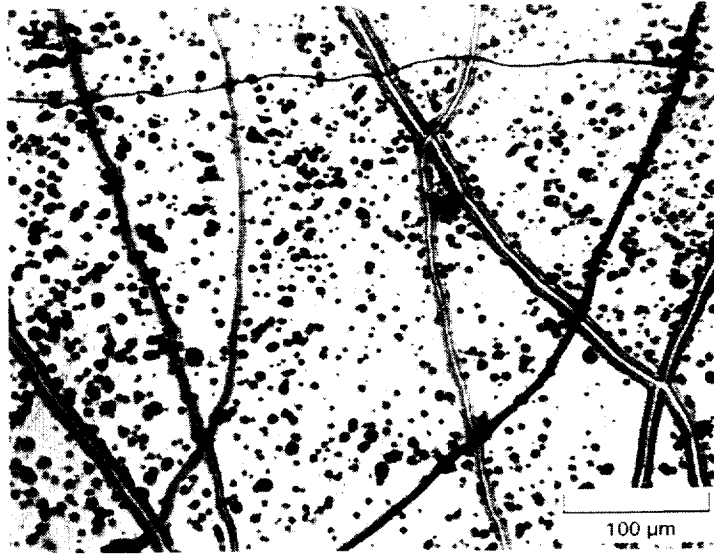
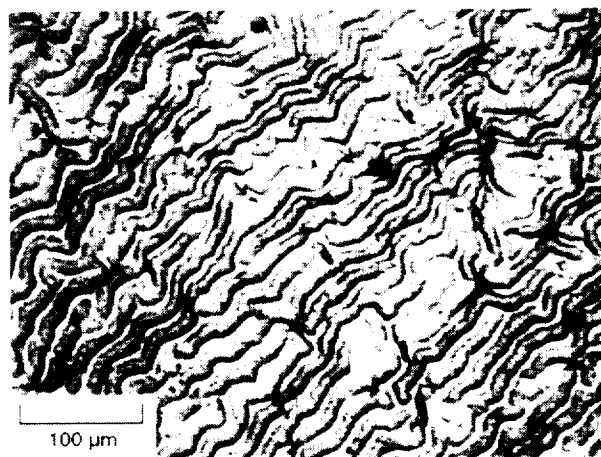Figure 3.—Optical micrograph of the 0.5 mm thick DC93-500 silicone samples exposed to a Kapton effective fluences of 1.0×10^{22} atoms/cm^2.

Figure 4.—Optical micrograph of the 12.7 μm thick CV2942 silicone samples exposed to a Kapton effective fluences of 1.2×10^{21} atoms/cm^2.
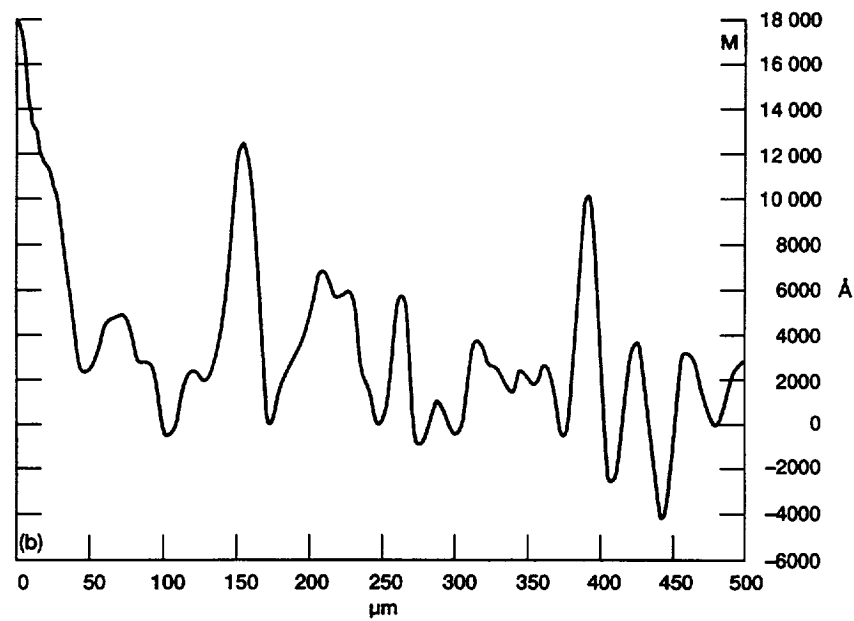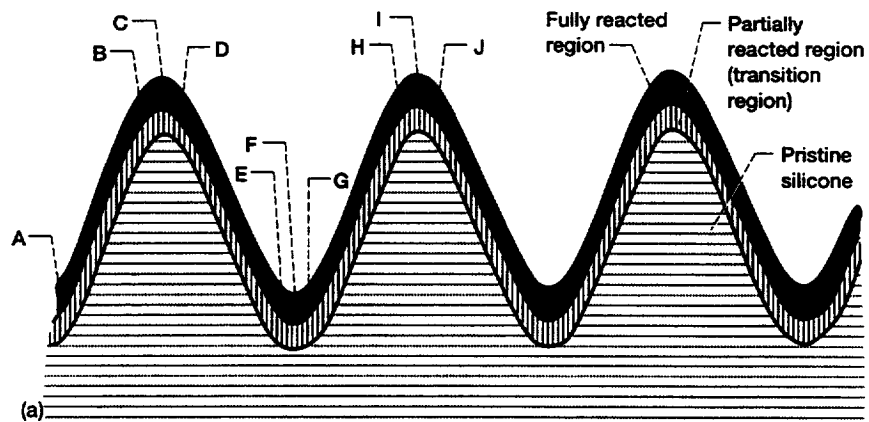
Figure 5.—(a) A model of rough silicone surface after atomic oxygen exposure. (b) Profilometer data from the surface of pristine DC93-500 silicone sample cured on a silicon waffer.
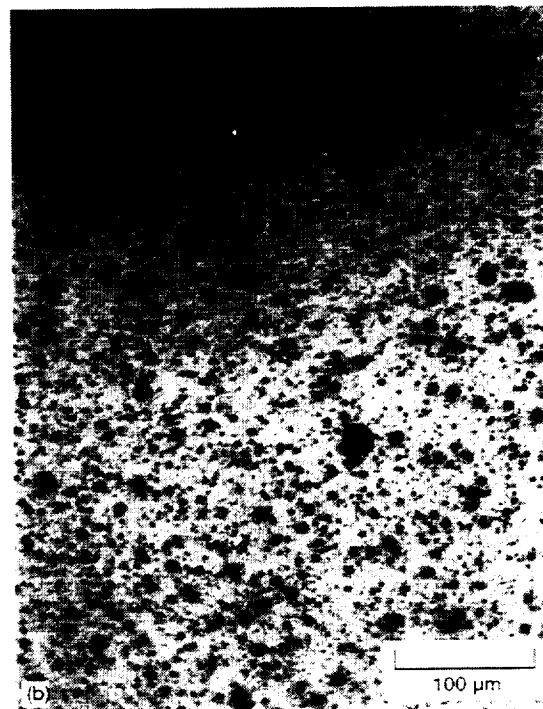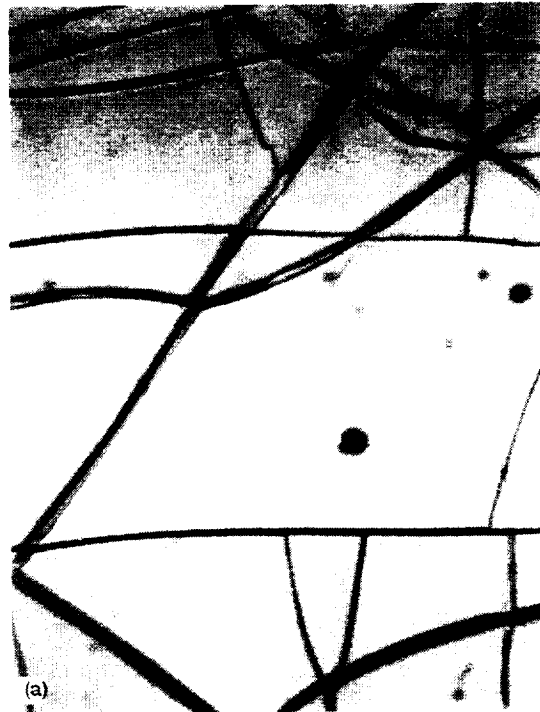
Figure 6.—Optical micrograph of thermal-energy atomic-
oxygen exposed DC93-500 silicone samples whose
surfaces are (a) smooth and (b) rough before the atomic
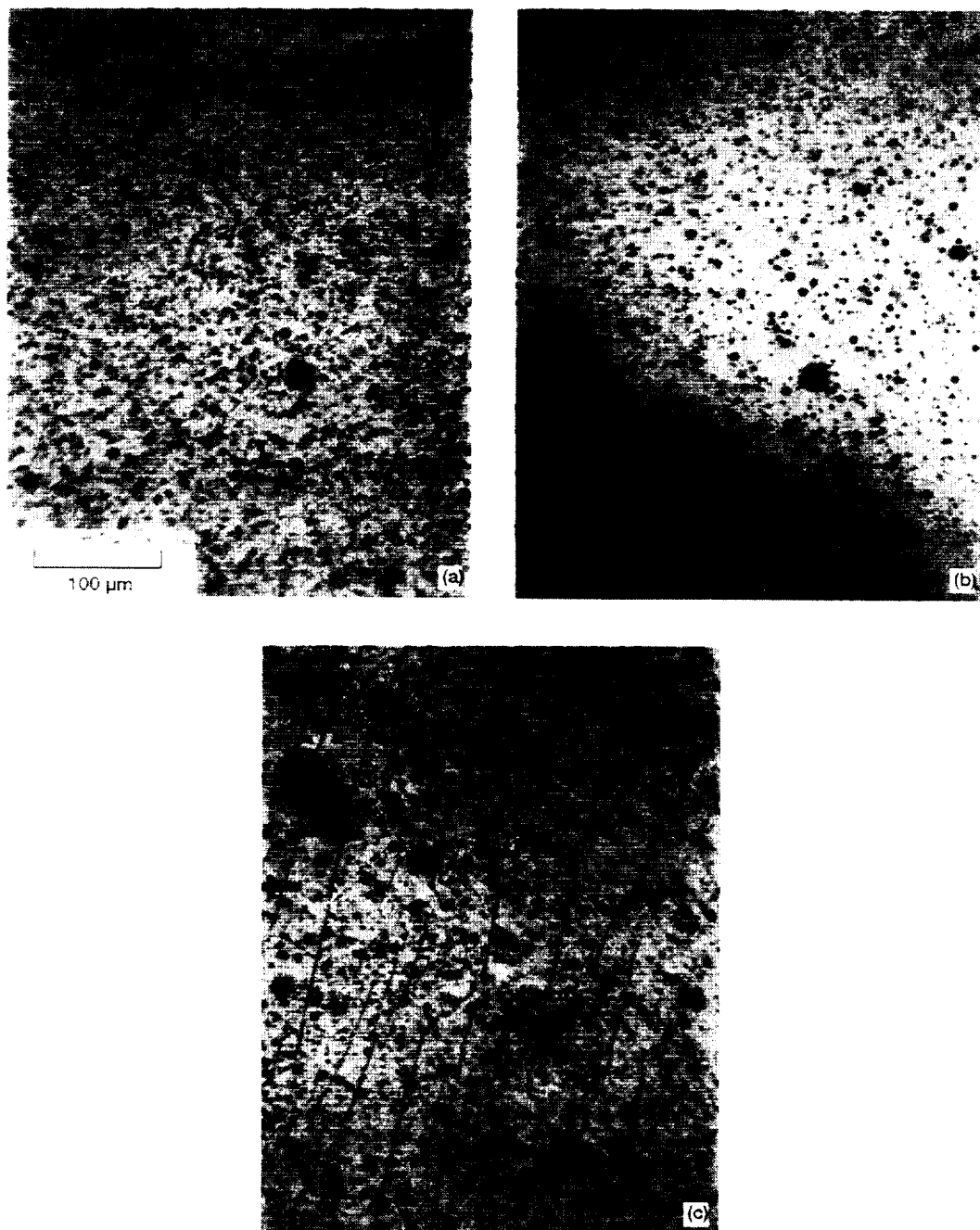oxygen exposure.

Figure 7.—Optical micrograph of the DC93-500 samples (a) cured on ion beam textured Kapton, (b) exposed to 1.5×10^{21} atom/cm^2 Kapton effective atomic oxygen fluence, and then (c) mechanically abused (quickly twisted by hand and tapping with hammer).

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13. ABSTRACT (Maximum 200 words)

Atomic-oxygen erosion on spacecraft in low Earth orbit is an issue which is becoming increasingly important because of the growing number of spacecraft that will fly in the orbits which have high concentrations of atomic oxygen. In this investigation, the atomic-oxygen durability of three types of electrical wire insulation (carbon-based, fluoropolymer, and polysiloxane elastomer) were evaluated. These insulation materials were exposed to thermal-energy atomic oxygen, which was obtained by RF excitation of air at a pressure of 11-20 Pa. The effects of atomic-oxygen exposure on insulation materials indicate that all carbon-based materials erode at about the same rate as polyimide Kapton and, therefore, are not atomic-oxygen durable. However, the durability of fluoropolymers needs to be evaluated on a case-by-case basis because the erosion rates of fluoropolymers vary widely. For example, experimental data suggest the formation of atomic fluorine during atomic-oxygen amorphous-fluorocarbon reactions. Dimethyl polysiloxanes (silicone) do not lose mass during atomic-oxygen exposure, but develop silica surfaces which are under tension and frequently crack as a result of loss of methyl groups. However, if the silicone sample surfaces were properly pretreated to provide a certain roughness, atomic oxygen exposure resulted in a sturdy, non-cracked atomic-oxygen durable SiO_2 layer. Since the surface does not crack during such silicone-atomic oxygen reaction, the crack-induced contamination by silicone can be reduced or completely stopped. Therefore, with proper pretreatment, silicone can be either a wire insulation material or a coating on wire insulation materials to provide atomic-oxygen durability.

14. SUBJECT TERMS

Atomic oxygen; Electrical wire insulators; Silicone; Fluoropolymer; Surface morphology

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